

Chapter 9 - Metal extraction and chemical reactivity

Metal reactions

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Checklist

Additional questions

You have already seen in Chapter 2, that metals usually have similar physical properties. However, they differ in other ways. Look closely at the three photographs in Figure 9.1.

Sodium is soft and reacts violently with both air and water. Iron also reacts with air and water but much more slowly, forming rust. Gold, however, remains totally unchanged after many hundreds of years. Sodium is said to be more reactive than iron and, in turn, iron is said to be more reactive than gold.

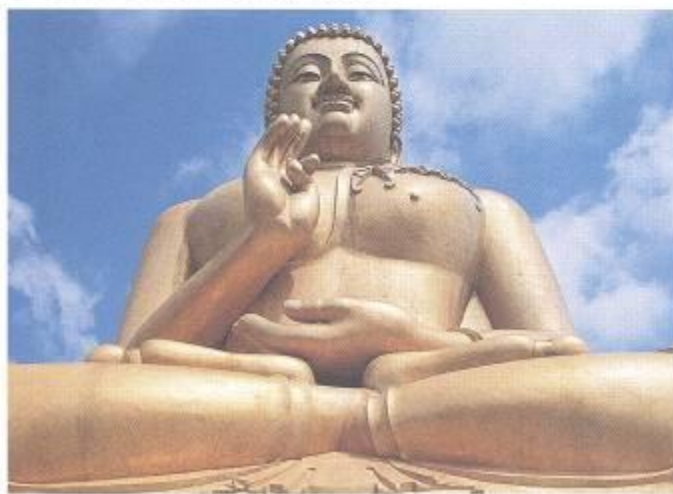


a Sodium burning in air/oxygen.

Figure 9.1



b Iron rusts when left unprotected.



c Gold is used in leaf form on this giant Buddha as it is unreactive.

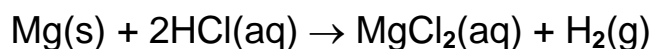
Metal reactions

By carrying out reactions in the laboratory with other metals and air, water and dilute acid, it is possible to produce an order of reactivity of the metals.

With acid

Look closely at the photograph in Figure 9.2 showing magnesium metal reacting with dilute hydrochloric acid. You will notice effervescence, which is caused by bubbles of hydrogen gas being formed as the reaction between the two substances proceeds. The other product of this reaction is the salt, magnesium chloride.

magnesium + hydrochloric acid \rightarrow magnesium chloride + hydrogen



If a metal reacts with dilute hydrochloric acid then hydrogen and the metal chloride are produced.

If similar reactions are carried out using other metals with acid, an order of reactivity can be produced. This is known as a **reactivity series**. An order of reactivity, giving the most reactive metal first, using results from experiments with dilute acid, is shown in Table 9.1. The table also shows how the metals react with air/oxygen and water/steam, and, in addition, the ease of extraction of the metal.



Figure 9.2 Effervescence occurs when magnesium is put into acid.

Table 9.1 Order of reactivity of metals.

Reactivity series	Reaction with dilute acid	Reaction with air/oxygen	Reaction with water	Ease of extraction
Potassium (K) Sodium (Na)	Produce H_2 with decreasing vigour ↓	Burn very brightly and vigorously ↓	Produce H_2 with decreasing vigour with cold water ↓	Difficult to extract ↓
Calcium (Ca) Magnesium (Mg)	↓	Burn to form an oxide with decreasing vigour ↓	React with steam with decreasing vigour ↓	Easier to extract ↓
Aluminium (Al*)	↓	↓	↓	↓
Zinc (Zn)	↓	↓	↓	↓
Iron (Fe)	↓	↓	↓	↓
Lead (Pb)	↓	React slowly to form the oxide ↓	Do not react with cold water or steam ↓	↓
Copper (Cu)	Do not react with dilute acids ↓	↓	↓	↓
Silver (Ag)	↓	Do not react ↓	↓	Found as the element (native) ↓
Gold (Au)	↓	↓	↓	↓
Platinum (Pt)	↓	↓	↓	↓

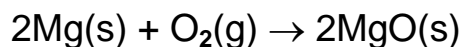
↑ Increasing reactivity of metal

* Because aluminium reacts so readily with the oxygen in the air, a protective oxide layer is formed on its surface. This often prevents any further reaction and disguises aluminium's true reactivity. This gives us the use of a light and strong metal.

With air/oxygen

Many metals react directly with oxygen to form oxides. For example, magnesium burns brightly in oxygen to form the white powder magnesium oxide.

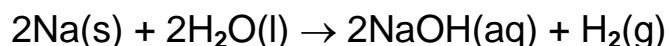
magnesium + oxygen → magnesium oxide



With water/steam

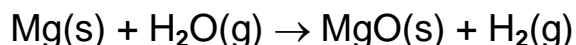
Reactive metals such as potassium, sodium and calcium react with cold water to produce the metal hydroxide and hydrogen gas. For example, the reaction of sodium with water produces sodium hydroxide and hydrogen.

sodium + water → sodium + hydrogen hydroxide



The moderately reactive metals, magnesium, zinc and iron, react slowly with water. They will, however, react more rapidly with steam (Figure 9.3). In their reaction with steam, the metal oxide and hydrogen are formed. For example, magnesium produces magnesium oxide and hydrogen gas.

magnesium + steam → magnesium + hydrogen oxide



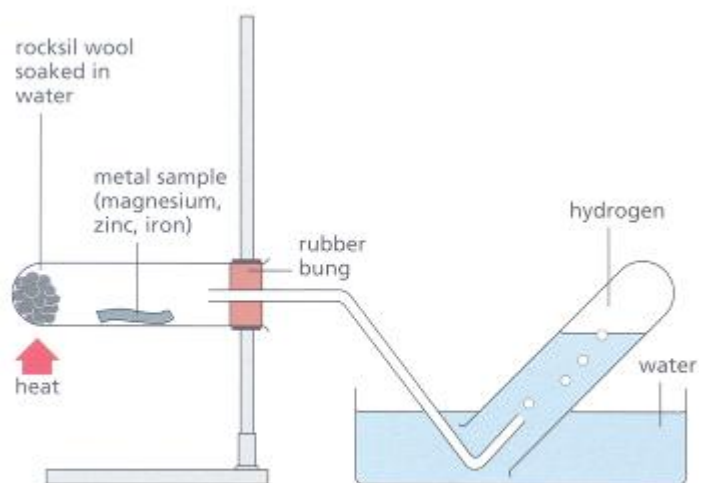


Figure 9.3 Apparatus used to investigate how metals such as magnesium react with steam.



a This stove is made of iron.



b Copper pots.

Figure 9.4



Figure 9.5 Concorde is made of an alloy which contains magnesium and aluminium.

Generally, it is the unreactive metals that we find the most uses for; for example, the metals iron and copper can be found in many everyday objects (Figure 9.4). However, magnesium is one of the metals used in the construction of Concorde (Figure 9.5).

Both sodium and potassium are so reactive that they have to be stored under oil to prevent them from coming into contact with water or air. However, because they have low melting points and are good conductors of heat, they are used as coolants for nuclear reactors.

Questions

1. Write balanced chemical equations for the reactions between:

- a. iron and dilute hydrochloric acid
- b. zinc and oxygen
- c. calcium and water.

2. Make a list of six things you have in your house made from copper or iron. Give a use for each of the other unreactive metals shown in the reactivity series.

Using the reactivity series

What predictions can be made using the reactivity series? It is useful in predicting how metals react.

Competition reactions in the solid state

If a more reactive metal is heated with the oxide of a less reactive metal, then it will remove the oxygen from it (as the oxide anion). You can see from the reactivity series that iron is less reactive than aluminium. If iron (III) oxide is mixed with aluminium and the mixture is heated using a magnesium fuse (Figure 9.6), a very violent reaction occurs as the competition between the aluminium and the iron for the oxygen takes place.

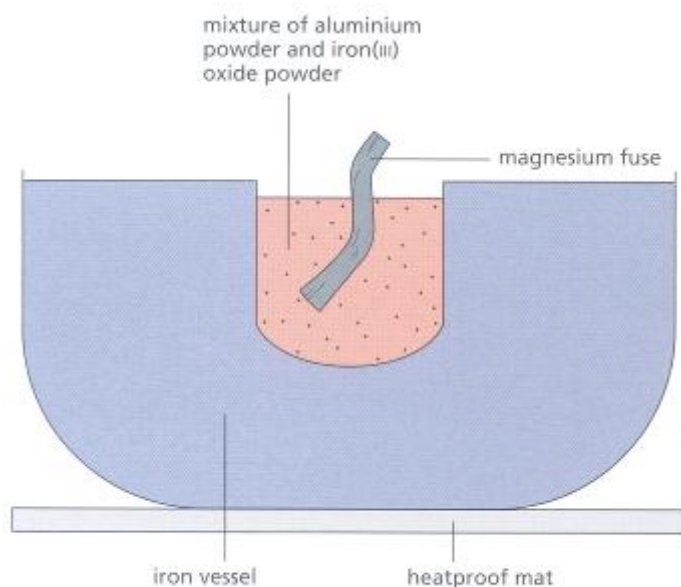
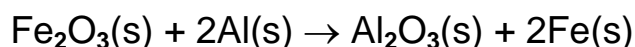
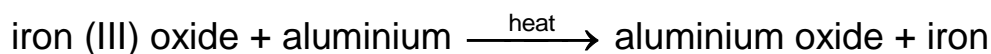


Figure 9.6 Thermite reaction mixture apparatus.

The aluminium, being the more reactive metal, takes the oxygen from the less reactive iron. It is a very exothermic reaction. When the reaction is over, a solid lump of iron is left along with a lot of white aluminium oxide powder.



This is a redox reaction (see Chapter 2 for a discussion of this type of reaction).

This particular reaction is known as the **Thermit reaction** (Figure 9.7). Since large amounts of heat are given out and the iron is formed in a molten state, this reaction is used to weld together damaged railway lines. It is also used in incendiary bombs (Figure 9.8).

Some metals, such as the transition metals chromium and titanium, are prepared from their oxides using this type of competition reaction.

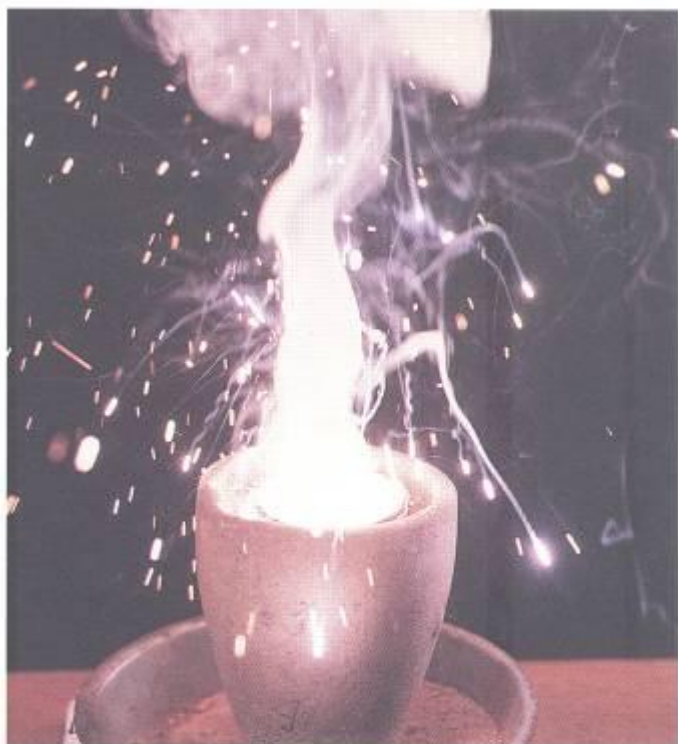


Figure 9.7 The Thermit reaction is used to weld damaged railway lines.



Figure 9.8 Incendiary bombs were used during World War II.

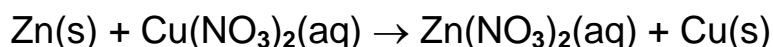
Competition reactions in aqueous solutions

In another reaction, metals compete with each other for other anions. This type of reaction is known as a **displacement reaction**. As in the previous type of competitive reaction, the reactivity series can be used to predict which of the metals will 'win'.

In a displacement reaction, a more reactive metal will displace a less reactive metal from a solution of its salt. Zinc is above copper in the reactivity series. Figure 9.9 shows what happens when a piece of zinc metal is left to stand in a solution of copper (II) nitrate.

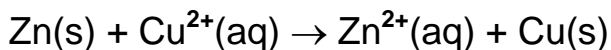
The copper (II) nitrate slowly loses its blue colour as the zinc continues to displace the copper from the solution and eventually becomes colourless zinc nitrate.

zinc + copper (II) nitrate → zinc nitrate + copper



The ionic equation for this reaction is:

zinc + copper ions → zinc ions + copper



This is also a redox reaction involving the transfer of two electrons from the zinc metal to the copper ions. The zinc is oxidised to zinc ions in aqueous solution, while the copper ions are reduced. (See Chapter 6 for a discussion of oxidation and reduction in terms of electron transfer.) It is possible to confirm the reactivity series for metals using competition reactions of the types discussed in this section.

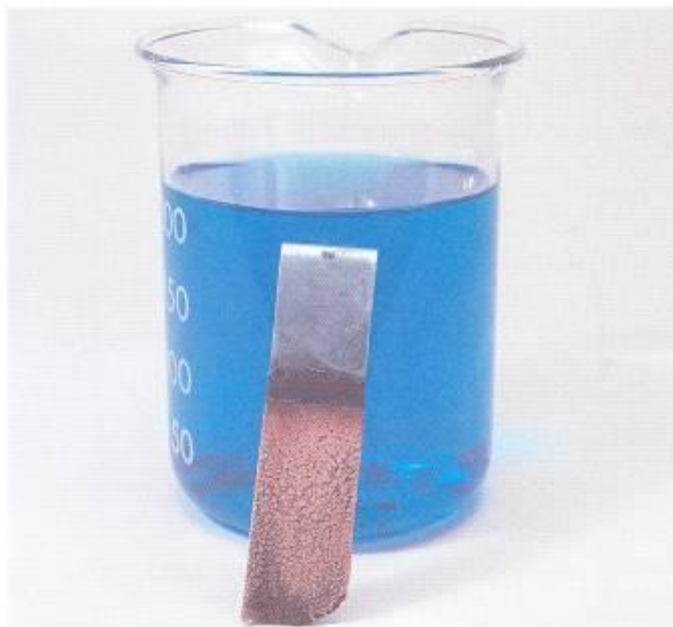


Figure 9.9 Zinc displaces copper.

Questions

1. Predict whether or not the following reactions will take place:

- a. magnesium + copper (II) oxide
- b. iron + aluminium oxide
- c. calcium + magnesium oxide.

Complete the word equations, and write balanced chemical and ionic equations for those reactions which do take place.

2. Predict whether or not the following reactions will take place:

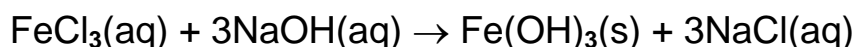
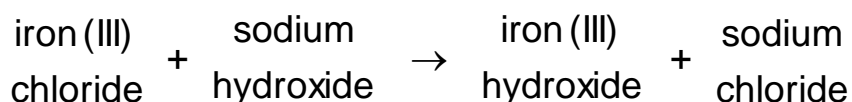
- a. magnesium + calcium nitrate solution
- b. iron + copper (II) nitrate solution
- c. copper + silver nitrate solution.

Complete the word equations, and write balanced chemical and ionic equations for those reactions which do take place.

Identifying metal ions

When an alkali dissolves in water, it produces hydroxide ions. It is known that most metal hydroxides are insoluble. So if hydroxide ions from a solution of an alkali are added to a solution of a metal salt, an insoluble, often coloured, metal hydroxide is precipitated from solution (Figure 9.10).

Let's take the example of iron(III) chloride with sodium hydroxide solution:



The ionic equation for this reaction is:

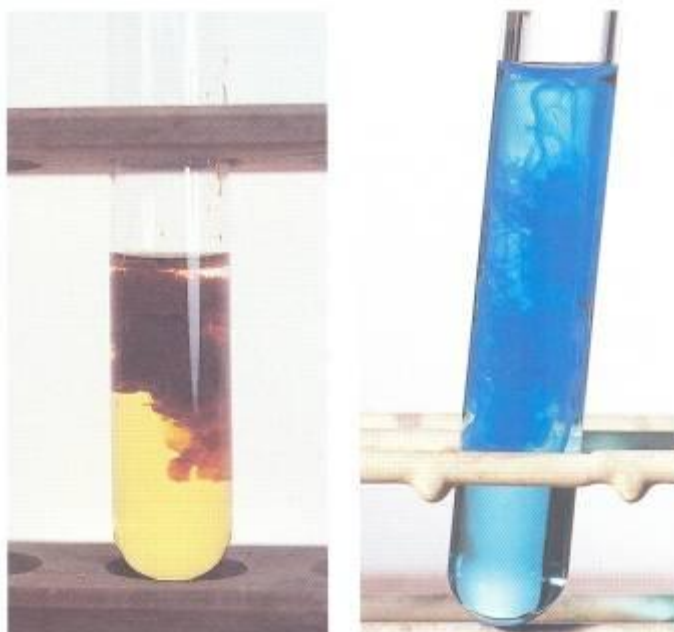
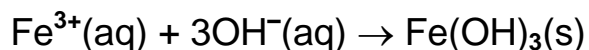


Figure 9.10 a Iron(III) hydroxide is precipitated. b Copper(II) hydroxide is precipitated.

Table 9.2 shows some of the colours of insoluble metal hydroxides. The

colours of these insoluble metal hydroxides can be used to identify the metal cations present in solution.

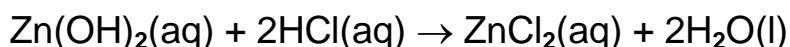
Table 9.2 Some of the colours of insoluble metal hydroxides.

Name	Formula	Colour of hydroxide
Aluminium hydroxide	$\text{Al}(\text{OH})_3$	White
Calcium hydroxide	$\text{Ca}(\text{OH})_2$	White
Copper (II) hydroxide	$\text{Cu}(\text{OH})_2$	Blue
Iron (II) hydroxide	$\text{Fe}(\text{OH})_2$	Green
Iron (III) hydroxide	$\text{Fe}(\text{OH})_3$	Brown (rust)
Zinc hydroxide	$\text{Zn}(\text{OH})_2$	White

Amphoteric hydroxides

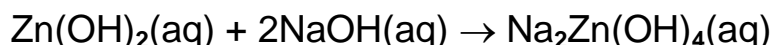
The hydroxides of metals are basic and they react with acids to form salts (Chapter 7). The hydroxides of some metals, however, will also react with strong bases, such as sodium hydroxide, to form soluble salts. Hydroxides of this type are said to be **amphoteric**. For example,

zinc hydroxide + hydrochloric acid \rightarrow zinc chloride + water



and

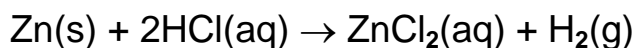
zinc hydroxide + sodium hydroxide \rightarrow sodium zincate



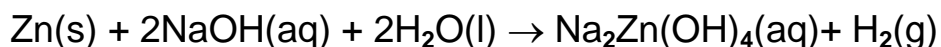
Other amphoteric hydroxides are lead hydroxide ($\text{Pb}(\text{OH})_2$) and aluminium hydroxide ($\text{Al}(\text{OH})_3$). We can use this sort of behaviour to help identify metal cations, as their hydroxides are soluble in strong bases.

Both aluminium and zinc metals will also react readily with moderately concentrated acids and alkalis. For example:

zinc + hydrochloric acid \rightarrow zinc chloride + hydrogen

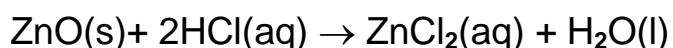


zinc + sodium hydroxide + water \rightarrow sodium zincate + hydrogen

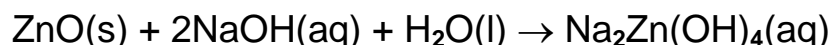


It should be noted that the oxides of the metals used as examples above are also amphoteric. Aluminium oxide and zinc oxide will react with both acids and alkalis.

zinc oxide + hydrochloric acid \rightarrow zinc chloride + water



zinc oxide + sodium hydroxide + water \rightarrow sodium zincate



Questions

1. Write equations for the reaction between:

a. aluminium and moderately concentrated hydrochloric acid

b. aluminium and moderately concentrated sodium hydroxide (producing sodium aluminate, NaAl(OH)_4).

2. Write ionic equations for the reactions which take place to produce the metal hydroxides shown in Table 9.2.

3. Describe what you would see when sodium hydroxide is added slowly to a solution containing iron (II) nitrate.

Discovery of metals

Metals have been used since prehistoric times. Many primitive iron tools have been excavated. These were probably made from small amounts of native iron found in rock from meteorites. It was not until about 2500 BC that iron became more widely used. This date marks the dawn of the iron age, when people learned how to get iron from its **ores** in larger quantities by reduction using charcoal. An ore is a naturally occurring mineral from which a metal can be extracted.

Over the centuries other metals, which like iron are also relatively low in the reactivity series, were isolated in a similar manner. These included copper, lead, tin and zinc. However, due to the relatively low abundance of the ores containing these metals, they were not extracted and used in large amounts.

Metals high in the reactivity series have proved very difficult to isolate. It was not until more recent times, through Sir Humphry Davy's work on electrolysis, that potassium (1807), sodium (1807), calcium (1808) and magnesium (1808) were isolated. Aluminium, the most plentiful reactive metal in the Earth's crust, was not extracted from its ore until 1827, by Friedrich Wohler, and the extremely reactive metal rubidium was not isolated until 1861 by Robert Bunsen and Gustav Kirchhoff.

Extraction of metals from their ores

The majority of metals are too reactive to exist on their own in the Earth's crust, and they occur naturally in rocks as compounds in ores (Figure 9.11). These ores are usually carbonates, oxides or sulphides of the metal, mixed with impurities.



Figure 9.11 Metal ores – chalcopyrite (left) and galena.

Some metals, such as gold and silver, occur in a native form as the free metal (Figure 9.12). They are very unreactive and have withstood the action of water and the atmosphere for many thousands of years without reacting to become compounds.



Figure 9.12 Gold crystals.

Table 9.3 Some common ores.

Metal	Name of ore	Chemical name of compound in ore	Formula	Usual method of extraction
Aluminium	Bauxite	Aluminium oxide	$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$	Electrolysis of oxide dissolved in molten cryolite
Copper	Copper pyrites	Copper iron sulphide	CuFeS_2	The sulphide ore is roasted in air
Iron	Haematite	Iron (III) oxide	Fe_2O_3	Heat oxide with carbon
Sodium	Rock salt	Sodium	NaCl	Electrolysis of molten

		chloride		sodium chloride
Zinc	Zinc blende	Zinc sulphide	ZnS	Sulphide is roasted in air and the oxide produced is heated with carbon

Some of the common ores are shown in Table 9.3.

Large lumps of the ore are first crushed and ground up by very heavy machinery. Some ores are already fairly concentrated when mined. For example, in some parts of the world, haematite contains over 80% Fe_2O_3 . However, other ores, such as copper pyrites, are often found to be less concentrated, with only 1% or less of the copper compound, and so they have to be concentrated before the metal can be extracted. The method used to extract the metal from its ore depends on the position of the metal in the reactivity series.

Extraction of reactive metals

Because reactive metals, such as sodium, hold on to the element(s) they have combined with, they are usually difficult to extract. For example, sodium chloride (as rock salt) is an ionic compound with the Na^+ and Cl^- ions strongly bonded to one another. The separation of these ions and the subsequent isolation of the sodium metal is therefore difficult.

Electrolysis of the molten, purified ore is the method used in these cases. During this process, the metal is produced at the cathode while a non-metal is produced at the anode. As you might expect, extraction of metal by electrolysis is expensive. In order to keep costs low, many metal smelters using electrolysis are situated in regions where there is hydroelectric power. Hydroelectric power is discussed further in Chapter 13.

For further discussion of the extraction of sodium and aluminium, see Chapter 6.

Extraction of fairly reactive metals

Metals towards the middle of the reactivity series, such as iron and zinc, may be extracted by reducing the metal oxide with the non-metal carbon.

Iron

Iron is extracted mainly from its oxides, haematite (Fe_2O_3) and magnetite (Fe_3O_4), in a blast furnace (Figures 9.13 and 9.14). These ores contain at least 60% iron. The iron ores used are a blend of those extracted in Australia, Canada, Sweden, Venezuela and Brazil. The blast furnace is a steel tower approximately 50 m high lined with heat-resistant bricks. It is loaded with the 'charge' of iron ore (usually haematite), coke (made by heating coal) and limestone (calcium carbonate).

A blast of hot air is sent in near the bottom of the furnace through holes (tuyeres) which makes the 'charge' glow, as the coke burns in the preheated air.

carbon + oxygen \rightarrow carbon dioxide

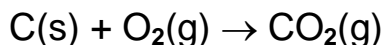


Figure 9.13 A blast furnace.

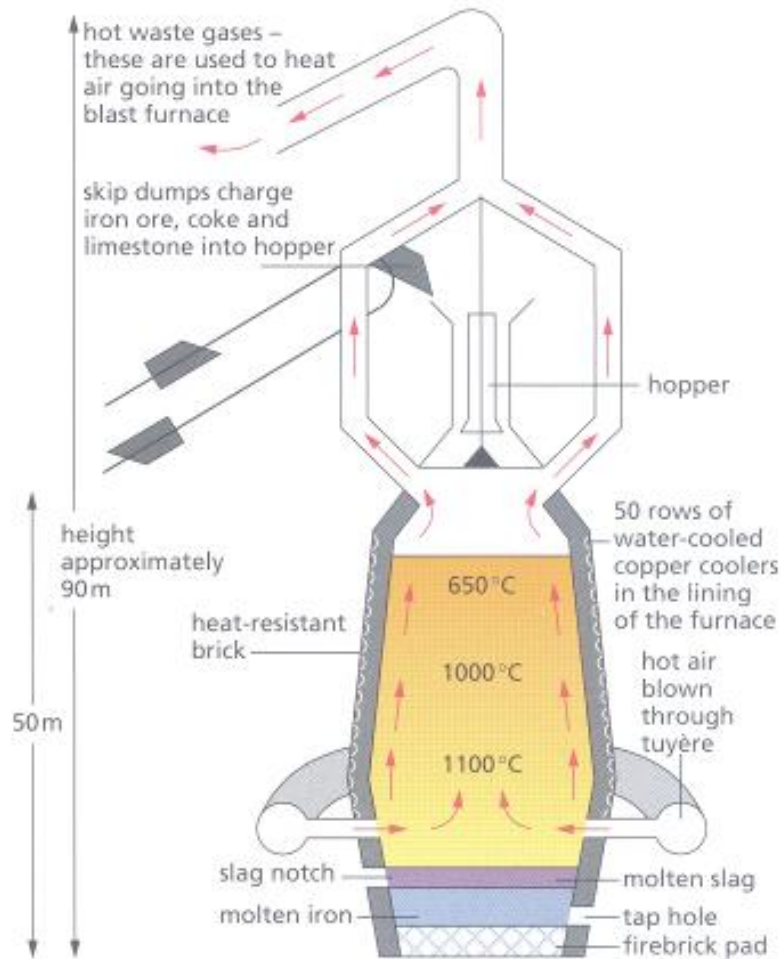


Figure 9.14 Cross-section of a blast furnace.

A number of chemical reactions then follow.

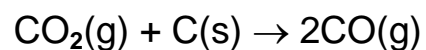
The limestone begins to decompose:

calcium carbonate \rightarrow calcium oxide + carbon dioxide



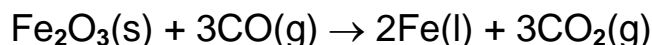
The carbon dioxide gas produced reacts with more hot coke higher up in the furnace, producing carbon monoxide in an endothermic reaction.

carbon dioxide + coke \rightarrow carbon monoxide



Carbon monoxide is a reducing agent. It rises up the furnace and reduces the iron(III) oxide ore. This takes place at a temperature of around 700 °C:

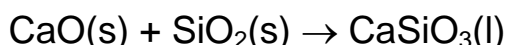
iron (III) oxide + carbon monoxide → iron + carbon dioxide



The molten iron produced trickles to the bottom of the furnace.

The calcium oxide formed from the limestone reacts with acidic impurities, for example silicon (IV) oxide (sand) (SiO_2), in the iron ore to form a liquid **slag**, which is mainly calcium silicate.

calcium oxide + silicon (IV) oxide → calcium silicate



This material also trickles to the bottom of the furnace, but because it is less dense than the molten iron, it floats on top of it. The molten iron, as well as the molten slag, may be **tapped off** (run off) at regular intervals.

The waste gases, mainly nitrogen and oxides of carbon, escape from the top of the furnace. They are used in a heat exchange process to heat incoming air and so help to reduce the energy costs of the process. Slag is the other waste material. It is used by builders and road makers (Figure 9.15) for foundations.

The extraction of iron is a continuous process and is much cheaper to run than an electrolytic method.

The iron obtained by this process is known as 'pig' or cast iron and contains about 4% carbon (as well as some other impurities). The name pig iron arises from the fact that if it is not subsequently converted into steel it is poured into moulds called pigs. Because of its brittle and hard nature, the iron produced by this process has limited use. Gas cylinders are sometimes made of cast iron, since they are unlikely to get deformed during their use.

The majority of the iron produced in the blast furnace is converted into different steel alloys (p. 141) such as manganese and tungsten steels as well as the well-known example of stainless steel (p. 140).

The annual production of iron worldwide is 560 million tonnes, 13.2 million tonnes of which are produced in the UK. The largest blast furnace in the UK is at Redcar in the north-east of England (Figure 9.16). This furnace is capable of producing 10 000 tonnes of iron per day.



Figure 9.15 Slag is used in road foundations.

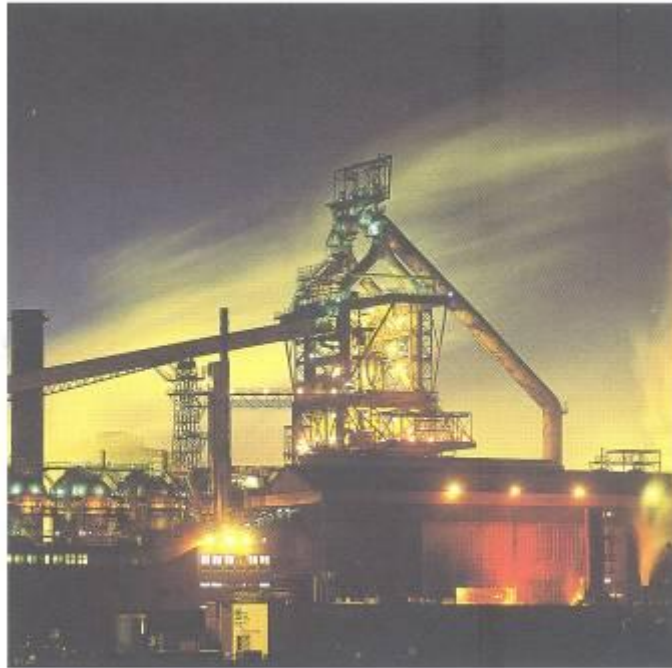


Figure 9.16 Redcar steelworks at Teeside, North Yorkshire.

Titanium

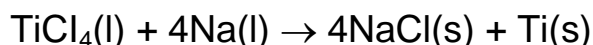
Titanium is the fourth most abundant structural metal after aluminium, iron and magnesium. It occurs naturally in the ores rutile (TiO_2) and ilmenite FeTiO_3 . However, the metal is mainly extracted from rutile. Titanium metal cannot be extracted successfully by electrolysis. The element of choice to reduce the oxide to the metal would be carbon since it is plentiful and cheap. However, rutile cannot be reduced by carbon or carbon monoxide or even hydrogen. Instead, TiO_2 is first converted to titanium (IV) chloride, TiCl_4 , which is covalently bonded and so cannot conduct electricity. It is then extracted by reaction with a more reactive metal, such as sodium. This makes titanium a very expensive metal since the sodium is produced by electrolysis and during the process it is converted to inexpensive sodium chloride.

The annual production of titanium is approximately 66000 tonnes, of which 6000 tonnes are produced in the UK. Titanium is a hard, silvery metal of low density. It is corrosion resistant (Figure 9.17). Titanium has many uses in the manufacture of strong, light alloys for use in aircraft, missile manufacture and car engines.

The metal is extracted by the following processes.

- The ore is processed to obtain pure titanium (IV) oxide, TiO_2 .
- The titanium (IV) oxide is converted to titanium (IV) chloride, TiCl_4 , by reaction with hydrochloric acid.
- The titanium(IV) chloride is purified by fractional distillation.
- Titanium metal is obtained from the reduction of titanium (IV) chloride by sodium or magnesium metals, at a temperature of approximately 1000°C in an argon atmosphere:

titanium chloride + sodium \rightarrow sodium chloride + titanium



- The reaction vessel or reactor is kept at the operating temperature for about four days before going through a cooling process for a further four days. The resulting mixture of titanium and sodium chloride is then crushed and mixed with dilute sulphuric acid. The sodium dissolves in the acid and can therefore be removed, leaving free titanium.

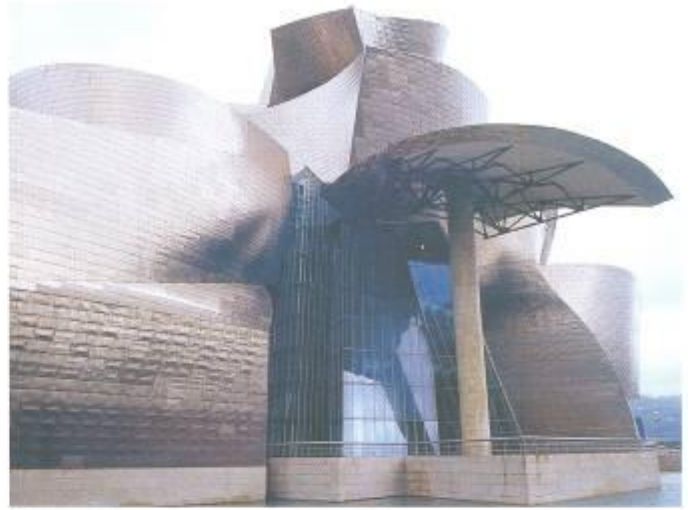


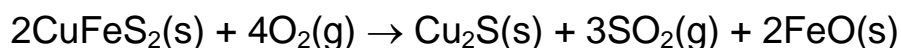
Figure 9.17 Titanium has a low density, resistance to corrosion and good mechanical strength. Titanium has been used to clad part of the Guggenheim Museum in Bilbao, Spain.

Extraction of unreactive metals

Copper

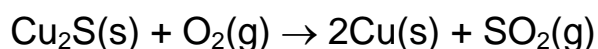
Copper is quite a long way down the reactivity series. It can be found as the free metal element or 'native' in the US. It is principally extracted, however, from copper pyrites, CuFeS_2 . The crushed ore is concentrated by froth flotation. A chemical known as a collector is added to an ore/water mixture and sticks to the surface of the copper pyrites particles, giving them a water-repellant coating. Detergent is added and air is blown into the mixture to make it froth. The copper pyrites particles are concentrated in the froth and can be removed easily. They are then roasted in a limited supply of air to ensure conversion of copper pyrites to copper (I) sulphide:

copper pyrites + oxygen \rightarrow copper (I) sulphide + sulphur dioxide + iron (II) oxide



Silicon is then added and the mixture is heated in the absence of air. The iron (II) oxide is converted into iron (II) silicate (FeSiO_3), which is run off. The remaining copper (I) sulphide is then reduced to copper by heating in a controlled amount of air.

copper (I) sulphide + oxygen \rightarrow copper + sulphur dioxide



Copper is then refined by electrolysis (Chapter 6) to give a product which is at least 99.92% pure. The purified copper is easily drawn into wires (it is highly ductile), which makes it useful for electrical wiring. It is also used in alloys, such as bronze and brass (Figure 9.18). Copper is also used to make water and central heating pipes, as well as steam boilers (it is a good conductor of heat).

The annual production of copper worldwide is 13.8 million tonnes; 1.8 million tonnes of this total is from recycling copper. In the UK the amount produced annually is 57 000 tonnes, which is all recycled copper.

Silver and gold

These are very unreactive metals. Silver exists mainly as silver sulphide, Ag_2S (silver glance). The extraction involves treatment of the pulverised ore with sodium cyanide. Zinc is then added to displace the silver from solution. The pure metal is obtained by electrolysis. Silver also exists to a small extent native in the Earth's crust. Gold is nearly always found in its native form (Figure 9.19). It is also obtained in significant amounts during both the electrolytic refining of copper and the extraction of lead.

Silver and gold, because of their resistance to corrosion, are used to make jewellery. Both of these metals are also used in the electronics industry because of their high electrical conductivity.



Figure 9.18 Copper is alloyed to produce brass.



Figure 9.19 This man is panning for gold.

Questions

1. How does the method used for extracting a metal from its ore depend on the metal's position in the reactivity series?
2. 'It is true to say that almost all the reactions by which a metal is extracted from its ore are reduction reactions.' Discuss this statement with respect to the extraction of iron, aluminium and zinc.
3. Zinc is extracted from zinc blende (ZnS). It is extracted in a furnace in a similar way to iron. Use your research skills, including the Internet, to suggest the detail of the extraction process.
4. In the reaction shown for the extraction of titanium from titanium (IV) chloride, write a word and symbol equation for the reduction of TiCl_4 with magnesium.

Recycling metals

Recycling 'banks' have become commonplace in recent years (Figure 9.20). Why should we really want to recycle metals? Certainly, if we extract fewer metals from the Earth then the existing reserves will last that much longer. Also, recycling metals prevents the creation of a huge environmental problem (Figure 9.21). However, one of the main considerations is that it saves money.

The main metals which are recycled include aluminium and iron. Aluminium is saved by many households as drinks cans and milk bottle tops, to be melted down and recast. Iron is collected at local authority tips in the form of discarded household goods and it also forms a large part of the materials collected by scrap metal dealers. Iron is recycled to steel. Many steel-making furnaces run mainly on scrap iron.

Aluminium is especially easy to recycle at low cost. Recycling uses only 5% of the energy needed to extract the metal by electrolysis from bauxite. Approximately 60% of the European need for aluminium is obtained by recycling.



Figure 9.20 Aluminium can recycling.



Figure 9.21 If we did not recycle metals, then this sight would be commonplace.

Rusting of iron

After a period of time, objects made of iron or steel will become coated with rust. The rusting of iron is a serious problem and wastes enormous amounts of money in the UK each year. It is estimated that upwards of £500 million a year is spent on replacing iron and steel structures.

Rust is an orange-red powder consisting mainly of hydrated iron(III) oxide ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$). Both water and oxygen are essential for iron to rust, and if one of these two substances is not present then rusting will not take place. The rusting of iron is encouraged by salt. Figure 9.22 shows an experiment to show that oxygen (from the air) and water are needed for iron to rust.

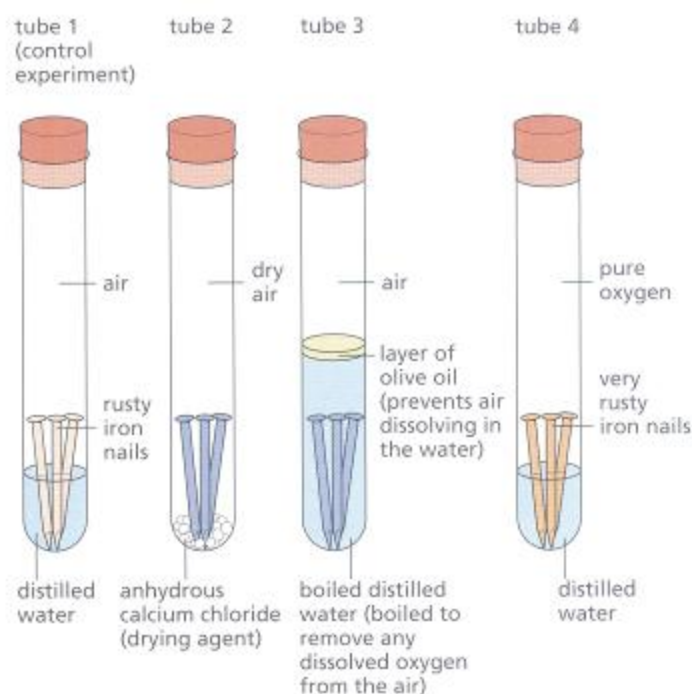


Figure 9.22 Rusting experiment with nails.

Rust prevention

To prevent iron rusting, it is necessary to stop oxygen (from the air) and water coming into contact with it. There are several ways of doing this.

Painting

Ships, lorries, cars, bridges and many other iron and steel structures are

painted to prevent rusting (Figure 9.23). However, if the paint is scratched, the iron beneath it will start to rust (Figure 9.24) and corrosion can then spread under the paintwork which is still sound. This is why it is essential that the paint is kept in good condition and checked regularly.

Oiling/greasing

The iron and steel in the moving parts of machinery are coated with oil to prevent them from coming into contact with air or moisture. This is the most common way of protecting moving parts of machinery, but the protective film must be renewed.

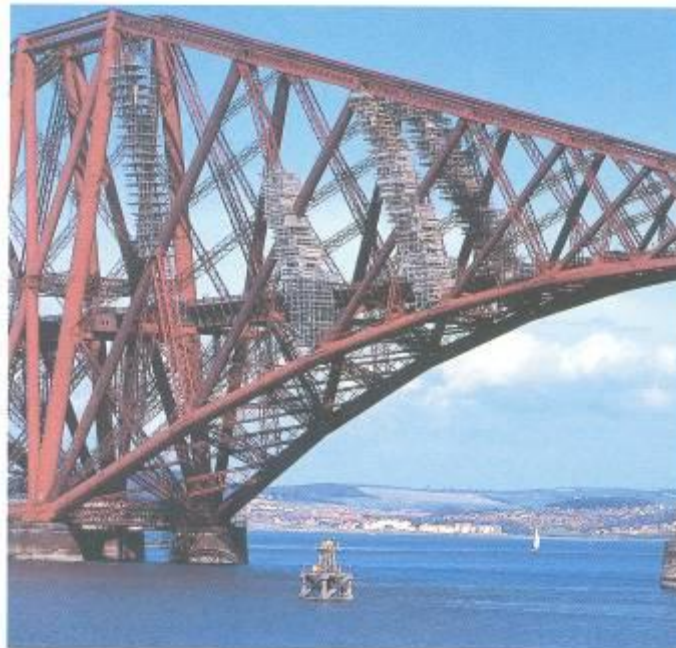


Figure 9.23 Painting keeps the air and water away from the steel structures of the Forth Rail Bridge.

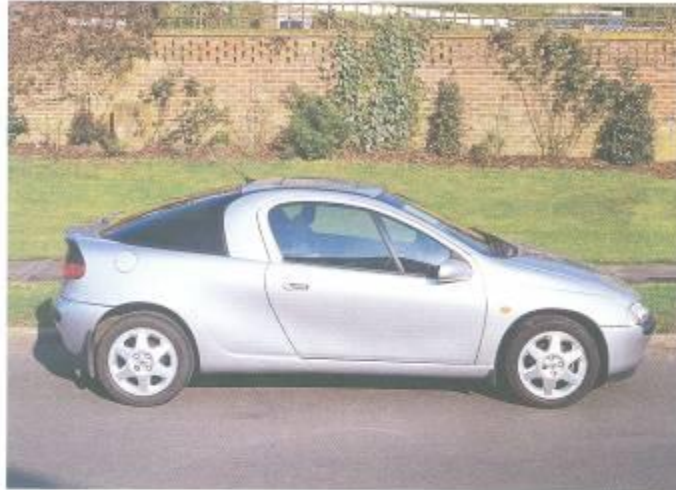


Figure 9.24 A brand new car is protected against corrosion (top). However, if the paintwork is damaged, then rusting will result.

Coating with plastic

The exteriors of refrigerators, freezers and many other items are coated with plastic, such as PVC, to prevent the steel structure rusting (Figure 9.25).



Figure 9.25 The coating of plastic stops the object coming into contact with oxygen or water.

Plating

Cans for food can be made from steel coated with tin. The tin is deposited on to the steel used to make food cans by dipping the steel into molten tin. Some car bumpers, as well as bicycle handlebars, are electroplated with chromium to prevent rusting. The chromium gives a decorative finish as well as protecting the steel beneath.

Galvanising

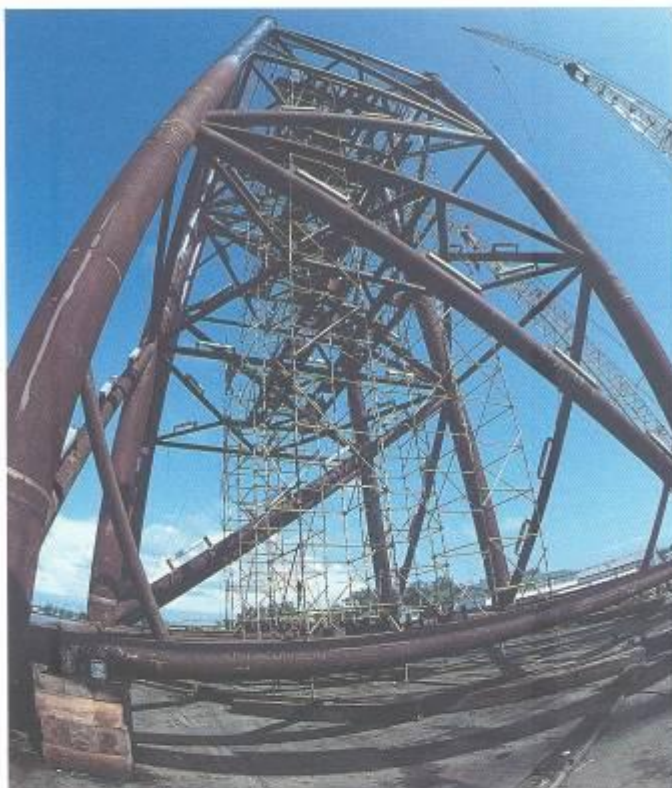
Some steel girders, used in the construction of bridges and buildings, are **galvanised**. Coal bunkers and steel dustbins are also galvanised. This involves dipping the object into molten zinc (Figure 9.26). The thin layer of the more reactive zinc metal coating the steel object slowly corrodes and loses electrons to the iron, thereby protecting it. This process continues even when much of the layer of zinc has been scratched away, so the iron continues to be protected.



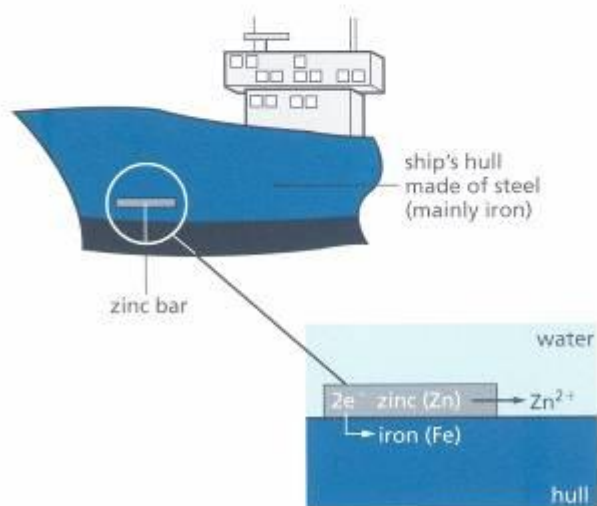
Figure 9.26 A metal object being galvanised.

Sacrificial protection

Bars of zinc are attached to the hulls of ships and to oil rigs (as shown in Figure 9.27a). Zinc is above iron in the reactivity series and will react in preference to it and so is corroded. As long as some of the zinc bars remain in contact with the iron structure, the structure will be protected from rusting. When the zinc runs out, it must be renewed. Gas and water pipes made of iron and steel are connected by a wire to blocks of magnesium to obtain the same result. In both cases, as the more reactive metal corrodes it loses electrons to the iron and so protects it (Figure 9.27b).



a Bars of zinc on an oil rig.



b The zinc is sacrificed to protect the steel. Electrons released from the dissolving zinc attract the Fe^{2+} ions back to the steel hull.

Figure 9.27 Examples of sacrificial protection.

Corrosion

Rusting is the most common form of corrosion. Corrosion is the name given to the process which takes place when metals and alloys are chemically attacked by oxygen, water or any other substances found in their immediate environment. The metals in the reactivity series will corrode to a greater or lesser extent. Generally, the higher the metal is in the reactivity series, the more rapidly it will corrode. If sodium and potassium were not stored under oil they would corrode very rapidly indeed. Magnesium, calcium and aluminium are usually covered by a thin coating of oxide after initial reaction with oxygen in the air. Freshly produced copper is pink in colour (see Figure 6.15). However, it soon turns brown due to the formation of copper (II) oxide on the surface of the metal.

In more exposed environments, copper roofs and pipes quickly become covered in verdigris. Verdigris is green in colour (Figure 9.28) and is composed of copper salts formed on copper. The composition of verdigris varies depending on the atmospheric conditions, but includes mixed copper(I) carbonate and copper(II) hydroxide ($\text{CuCO}_3 \cdot \text{Cu(OH)}_2$).

Gold and platinum are unreactive and do not corrode, even after thousands of years.

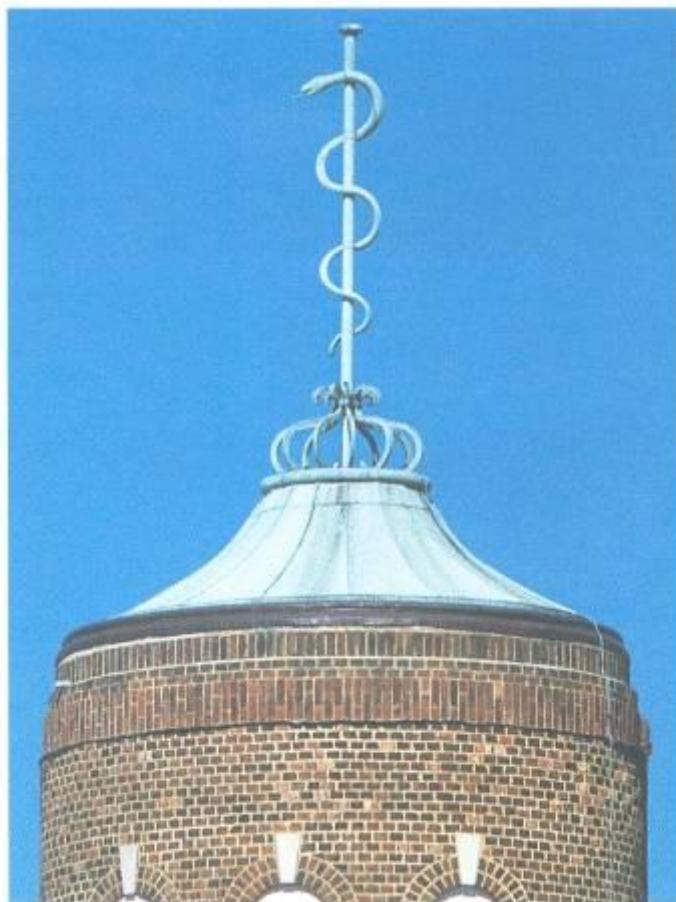


Figure 9.28 Verdigris soon covers copper roofs in exposed environments.

Questions

1. What is rust? Explain how rust forms on structures made of iron or steel.
2. Rusting is a redox reaction. Explain the process of rusting in terms of oxidation and reduction (Chapter 6).
3. Design an experiment to help you decide whether steel rusts faster than iron.
4. Why do car exhausts rust faster than other structures made of steel?

Alloys

The majority of the metallic substances used today are **alloys**. Alloys are mixtures of two or more metals and are formed by mixing molten metals thoroughly. It is generally found that alloying produces a metallic substance that has more useful properties than the original pure metals it was made from. Steel, which is a mixture of the metal iron and the non-metal carbon, is also considered to be an alloy.

Of all the alloys we use, steel is perhaps the most important. Many steels have been produced; they contain not only iron but also carbon and other metals. For example, nickel and chromium are the added metals when stainless steel is produced (Figure 9.29). The chromium prevents the steel from rusting while the nickel makes it harder.



Figure 9.29 A stainless steel exhaust system. Why do you think more people are buying these exhaust systems?

Production of steel

The 'pig iron' obtained from the blast furnace contains between 3% and 5% of carbon and other impurities, such as sulphur, silicon and phosphorus. These impurities make the iron hard and brittle. In order to improve the quality of the metal, most of the impurities must be removed and in doing this, steel is produced.

The impurities are removed in the **basic oxygen process**, which is the most important of the steel-making processes. In this process:

- Molten pig iron from the blast furnace is poured into the basic oxygen furnace (Figure 9.30).
- A water-cooled 'lance' is introduced into the furnace and oxygen at 5-15 atm pressure is blown onto the surface of the molten metal.
- Carbon is oxidised to carbon monoxide and carbon dioxide, while sulphur is oxidised to sulphur dioxide. These escape as gases.
- Silicon and phosphorus are oxidised to silicon (IV) oxide and phosphorus pentoxide, which are solid oxides.
- Some calcium oxide (lime) is added to remove these solid oxides as slag. The slag may be skimmed or poured off the surface.
- Samples are continuously taken and checked for carbon content. When the required amount of carbon has been reached, the blast of oxygen is turned off.

The basic oxygen furnace can convert up to 300 tonnes of pig iron to steel per hour.

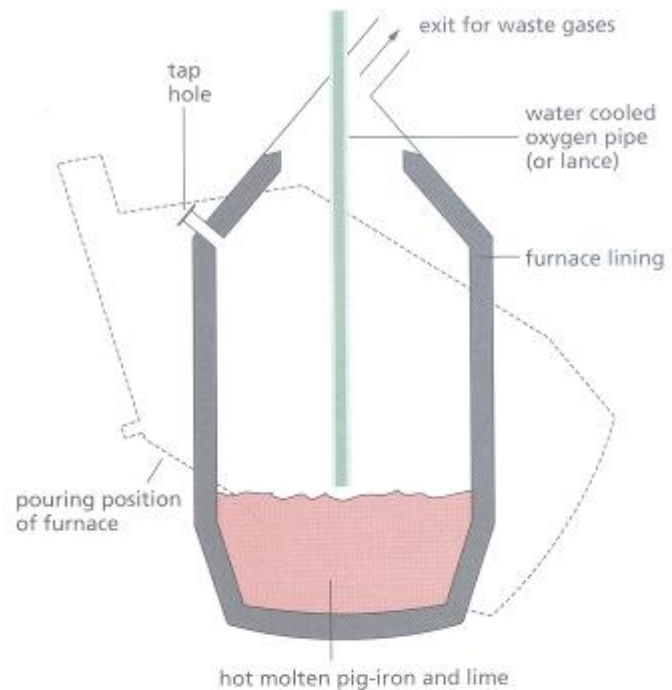
Worldwide production by this process is 430 million tonnes. The UK produces 14 million tonnes.

There are various types of steel that differ only in their carbon content. The differing amounts of carbon present confer different properties on the steel and they are used for different purposes (Table 9.4). If other types of steel

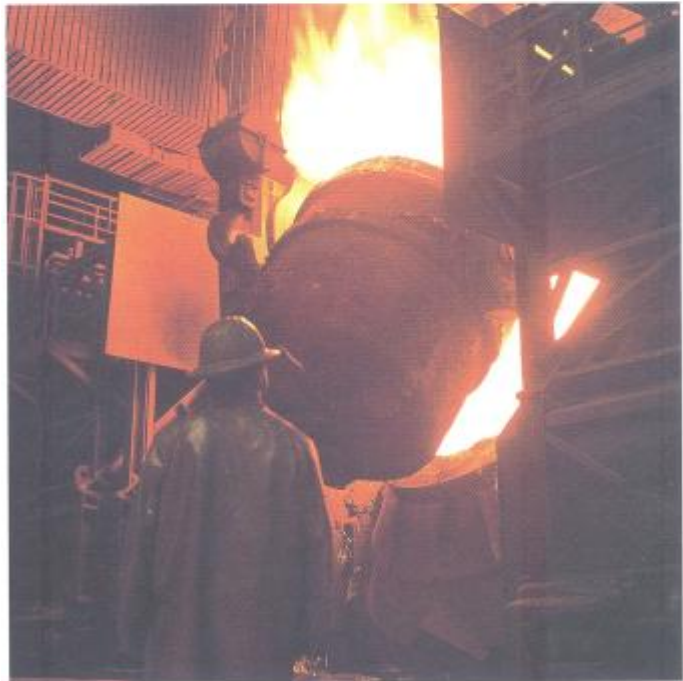
are required then up to 30% scrap steel is added, along with other metals (such as tungsten), and the carbon is burned off.

Steel recycling

The recycling of scrap steel contributes 310 million tonnes to the world supply of the alloy – 750 million tonnes. It has been calculated that the energy savings are equivalent to 160 million tonnes of coal. Also, it has been calculated that the raw materials conserved are equivalent to 200 million tonnes of iron ore.



a A section through the basic oxygen furnace.



b Basic oxygen furnace.

Figure 9.30

Table 9.4 Different types of steel.

Steel	Typical composition	Properties	Uses
Mild steel	99.5% iron, 0.5% carbon	Easily worked Lost most of brittleness	Car bodies, large structures
Hard steel	99% iron, 1% carbon	Tough and brittle	Cutting tools, chisels, razor blades
Manganese steel	87% iron, 13% manganese	Tough, springy	Drill bits, springs
Stainless steel	74% iron, 18% chromium, 8% nickel	Tough, does not corrode	Cutlery, kitchen sinks, surgical instruments
Tungsten steel	95% iron, 5% tungsten	Tough, hard, even at high	Edges of high- speed cutting tools temperatures

Alloys to order

Just as the properties of iron can be changed by alloying, so the same can be done with other useful metals. Metallurgists have designed alloys to suit a wide variety of different uses. Many thousands of alloys are now made, with the majority being 'tailor-made' to do a particular job (Figure 9.31).

Table 9.5 shows some of the more common alloys, together with some of their uses.

Table 9.5 Uses of common alloys.

Alloy	Composition	Use
Brass	65% copper, 35% zinc	Jewellery, machine bearings, electrical connections, door furniture
Bronze	90% copper, 10% tin	Castings, machine parts

Cupro-nickel	30% copper, 70% nickel	Turbine blades
	75% copper, 25% nickel	Coinage metal
Duralumin	95% aluminium, 4% copper, 1% magnesium, manganese and iron	Aircraft construction, bicycle parts
Magnalium	70% aluminium, 30% magnesium	Aircraft construction
Pewter	30% lead, 70% tin, a small amount of antimony	Plates, ornaments and drinking mugs
Solder	70% lead, 30% tin	Connecting electrical wiring

Questions

1. Calcium oxide is a base. It combines with solid, acidic oxides in the basic oxygen furnace.

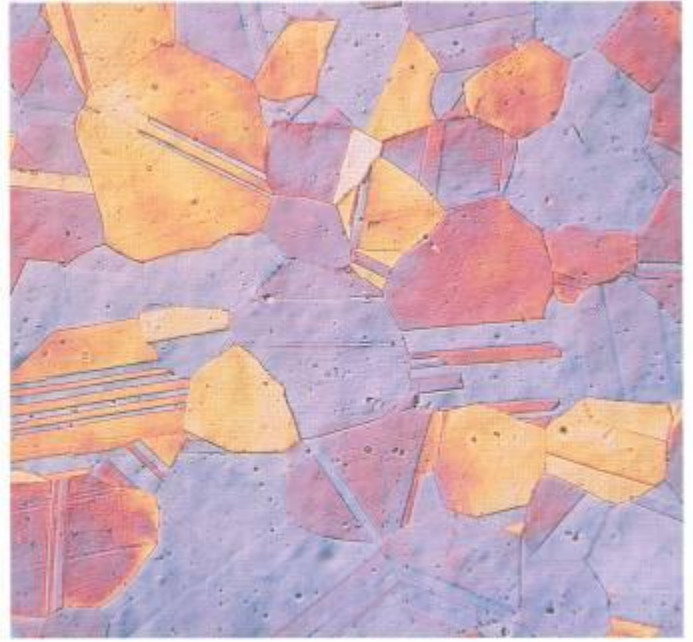
Write a chemical equation for one of these oxides reacting with the added lime.

2. 'Many metals are more useful to us when mixed with some other elements.' Discuss this statement with respect to stainless steel.



a Bronze is often used in sculptures.

Figure 9.31



b A polarised light micrograph of brass showing the distinct grain structure of this alloy.

Checklist

After studying Chapter 9 you should know and understand the following terms.

Alloy Generally, a mixture of two or more metals (for example, brass is an alloy of zinc and copper) or a metal and a non-metal (for example, steel is an alloy of iron and carbon, sometimes with other metals included). They are formed by mixing the molten substances thoroughly. Generally, it is found that alloying produces a metallic substance which has more useful properties than the original pure metals it was made from.

Amphoteric hydroxide A hydroxide which can behave as an acid (react with an alkali) or a base (react with an acid), for example zinc hydroxide.

Blast furnace A furnace for smelting iron ores such as haematite (Fe_2O_3) and magnetite (Fe_3O_4) to produce pig (or cast) iron. In a modified form it can be used to extract metals such as zinc.

Competition reactions Reactions in which metals compete for oxygen or anions. The more reactive metal:

- takes the oxygen from the oxide of a less reactive metal
- displaces the less reactive metal from a solution of that metal salt - this type of competition reaction is known as a displacement reaction.

Corrosion The name given to the process that takes place when metals and alloys are chemically attacked by oxygen, water or any other substances found in their immediate environment.

Metal extraction The method used to extract a metal from its ore depends on the position of the metal in the reactivity series.

- Reactive metals are usually difficult to extract. The preferred method is by electrolysis of the molten ore (electrolytic reduction); for example, sodium from molten sodium chloride.
- Moderately reactive metals (those near the middle of the reactivity series) are extracted using a chemical reducing agent (for example

carbon) in a furnace; for example, iron from haematite in the blast furnace.

- Unreactive metals, for example gold and silver, occur in an uncombined (native) state as the free metal.

Metal ion precipitation These are reactions in which certain metal cations form insoluble hydroxides. The colours of these insoluble hydroxides can be used to identify the metal cations which are present; for example, copper (II) hydroxide is a blue precipitate.

Ore A naturally occurring mineral from which a metal can be extracted.

Reactivity series of metals An order of reactivity, giving the most reactive metal first, based on results from experiments with oxygen, water and dilute hydrochloric acid.

Recycling metals Metal drink cans such as those made of aluminium are collected in large 'banks' for the sole purpose of recycling them. Reusing the metal in this way saves money.

Rust A loose, orange-brown, flaky layer of hydrated iron (III) oxide found on the surface of iron or steel. The conditions necessary for rusting to take place are the presence of oxygen and water. The rusting process is encouraged by other substances such as salt. It is an oxidation process.

Rust prevention To prevent iron rusting it is necessary to stop oxygen and water coming into contact with it. The methods employed include painting, oiling/greasing, coating with plastic, plating, galvanising and sacrificial protection.

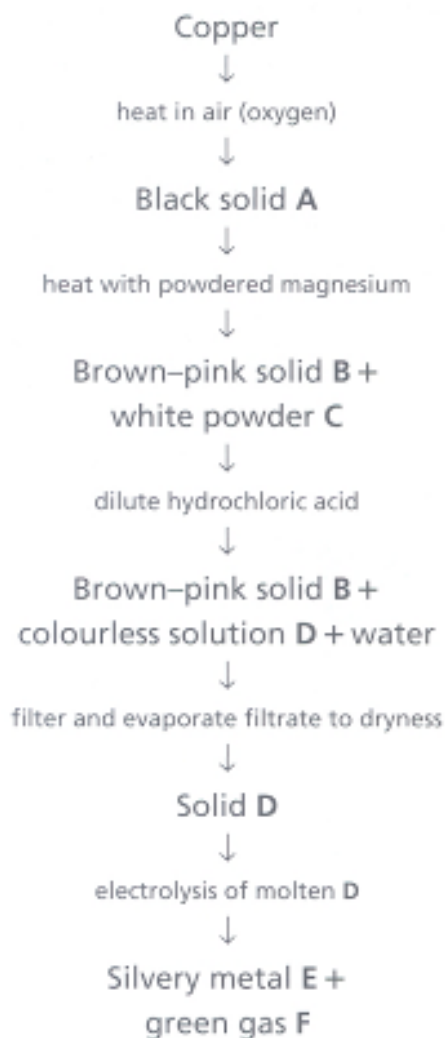
Metal extraction and chemical reactivity

Additional questions

1. Use the following list of metals to answer the questions a to i: iron, calcium, potassium, gold, aluminium, magnesium, sodium, zinc, platinum.

- a. Which of the metals is found native?
- b. Which of the metals is found in nature as the ore:
 - (i) rock salt?
 - (ii) rutile?
- c. Which metal has a carbonate found in nature called chalk?
- d. Which of the metals will not react with oxygen to form an oxide?
- e. Which of the metals will react violently with cold water?
- f. Choose one of the metals in your answer to e and write a balanced chemical equation for the reaction which takes place.
- g. Which of the metals has a protective oxide coating on its surface?
- h. Which of the metals reacts very slowly with cold water but extremely vigorously with steam?
- i. Which of the metals is used to galvanise iron?

2.



a. Name and give the formulae of the substances A to F.

b. Write balanced chemical equations for the reactions in which:

- (i) black solid A was formed
- (ii) white powder C and brown-pink solid B were formed
- (iii) colourless solution D was formed.

c. The reaction between black solid A and magnesium is a redox reaction. With reference to this reaction, explain what you understand by this statement.

d. Write anode and cathode reactions for the processes which take place during the electrolysis of molten D.

e. Suggest a use for:

- (i) brown-pink solid B
- (ii) silvery metal E
- (iii) green gas F.

3. Explain the following:

- a. metals such as gold and silver occur native in the Earth's crust
- b. the parts of shipwrecks made of iron rust more slowly in deep water
- c. zinc bars are attached to the structure of oil rigs to prevent them from rusting
- d. copper roofs quickly become covered with a green coating when exposed to the atmosphere
- e. recycling metals can save money.

4. Iron is extracted from its ores haematite and magnetite. Usually it is extracted from haematite (iron (III) oxide). The ore is mixed with limestone and coke and reduced to the metal in a blast furnace. The following is a brief outline of the reactions involved.



- Name the gases X and Y.
- Give a chemical test to identify gas X.
- Write balanced chemical equations for the reactions shown above.
- The added limestone is involved in the following reactions:



- Give the chemical names for limestone and slag.
 - Write balanced chemical equations for the reactions shown above.
 - Why is the reaction between calcium oxide and silicon(IV) oxide called an acid-base reaction?
 - Describe what happens to the liquid iron and slag when they reach the bottom of the furnace.
- Why do you think that the furnace used in the extraction of iron is called a blast furnace?

5. The iron obtained from the blast furnace is known as pig or cast iron. Because of the presence of impurities, such as carbon, it has a hard and brittle nature. Most of this type of iron is therefore converted into steel in the basic oxygen process. During this process either all or some of the carbon is removed. Calculated quantities of other elements are then added to produce the required type of steel.

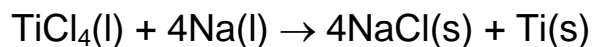
- a. Explain the meaning of the term alloy as applied to steel.
- b. Name two impurities, other than carbon, which are present in cast iron and which are removed completely during the steel manufacture.
- c. Describe the method of steel manufacture used which removes the impurities referred to in b.
- d. Name two metallic elements which may be added to the basic oxygen furnace to produce different varieties of steel.
- e. Give two uses of stainless steel.
- f. Give two advantages of stainless steel compared with cast iron.

6. The metal titanium is extracted from its ore rutile (TiO_2).

a. Describe the processes involved in the extraction of titanium from rutile.

b. Name the area of the periodic table in which titanium is found.

c. The final part of the process involves the following reaction:

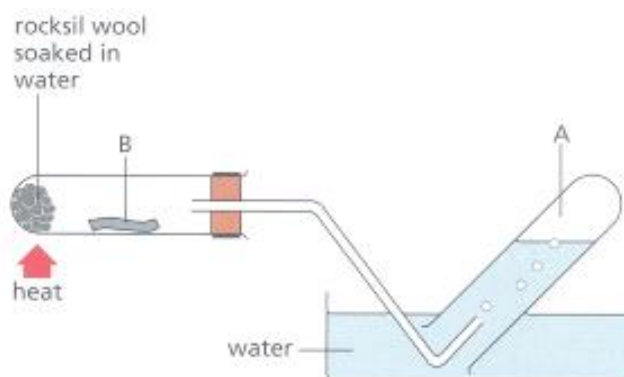


(i) Calculate the quantity of titanium produced from 19 tonnes of titanium (IV) chloride (TiCl_4).

(ii) How much sodium would have to be used to extract the titanium from the 19 tonnes of TiCl_4 used in (i)?

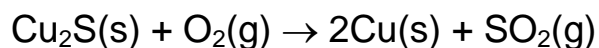
d. Give two uses of titanium metal.

7. Zinc can be reacted with steam using the apparatus shown below. When gas A is collected, mixed with air and ignited it gives a small pop. A white solid B remains in the test tube when the reaction has stopped and the apparatus cooled down.



- a. Name and give the formula of gas A.
- b. (i) Name the product formed when gas A burns in air.
(ii) Write a balanced chemical equation for this reaction.
- c. (i) Name white solid B.
(ii) Write a balanced chemical equation to represent the reaction between magnesium and steam.
- d. Name two other metals which could be safely used to replace zinc and produce another sample of gas A.
- e. When zinc reacts with dilute hydrochloric acid, gas A is produced again. Write a balanced chemical equation to represent this reaction and name the other product of this reaction.

8. Copper is extracted in the final stage by roasting copper (I) sulphide (Cu_2S) in a current of air. This converts the sulphide to the metal.



a. (i) What is the name of the chemical process by which copper (I) sulphide is converted to copper?

(ii) At what temperature does this process take place?

b. It is a very expensive business to maintain the high temperature needed to efficiently convert copper (I) sulphide to copper. How are the heating costs offset?

c. Calculate the quantity of copper (I) sulphide required to produce 1270 tonnes of copper. (A_r : O = 16; S = 32, Cu = 63.5)

d. For use in electrical wiring, the copper must be 99.99% pure. How is the copper purified to obtain this high purity?